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Title: Plasma Sprayed Zirconium Diffusion Barrier Development for Monolithic U-Mo Metallic Fuels

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Plasma Sprayed Zirconium Diffusion Barrier Development for Monolithic U-Mo Metallic Fuel

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Sigma Division (formerly MST-6)

James Smith PostDoc/Early Career Talk
July 11 – 15, 2016
UNCLASSIFIED LA-UR-xxxxxx

Outline

- **DOE/NNSA CONVERT Program**
- **Plasma Spraying**
- **Zr on U-10Mo**
  - Zr-U Interface
  - Bond Strength
  - Oxidation and Heat Treatments
- **Crystal Phase using Neutron Diffraction**
- **Conclusions**

NA-21/NA-23 Global Threat Reduction Initiative (GTRI) Program
"Remove as much HEU as possible"

GTRI MISSION

Reduce and protect vulnerable nuclear and radiological material located at civilian sites worldwide *by providing support for countries' own national programs*

A National Priority

"Lead a global effort to secure all nuclear weapons materials at vulnerable sites within four years"

President Barack Obama

GTRI is:

- A part of President Obama's comprehensive strategy to prevent nuclear terrorism;
- The key organization responsible for implementing the U.S. HEU minimization policy.

Convert

Convert research reactors from the use of highly enriched uranium (HEU) to low enriched uranium (LEU)

These efforts result in permanent threat reduction by minimizing and, to the extent possible, eliminating the need for HEU in civilian applications – each reactor converted or shut down eliminates a source of bomb material.

Remove

nove and dispose of ess nuclear and ological materials; and

se efforts result in nanent threat reduction liminating bomb erial at civilian sites – n kilogram or curie of dangerous material that moved reduces the risk terrorist bomb.

Protect

Protect high priority nuclear and radiological materials from theft and sabotage

These efforts result in threat reduction by improving security on the bomb material remaining at civilian sites – each vulnerable building that is protected reduces the risk until a permanent threat reduction solution can be implemented.

US Dept of Energy CONVERT Program

- In 2011, at a joint meeting of U.S. National Academy of Sciences and Russian Academy of Sciences, former NNSA Administrator D'Agostino commented that the conversion of research reactors to using low enriched uranium (LEU) is "a vital international security issue" and "vital to the nuclear security agenda outlined by our two presidents"
- US and Russia agree, but who will take the lead? Also, no new fuels certified in 30 years…

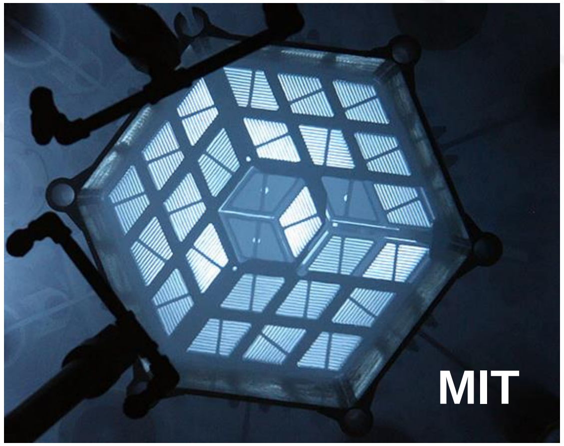
Российская Академия Наук

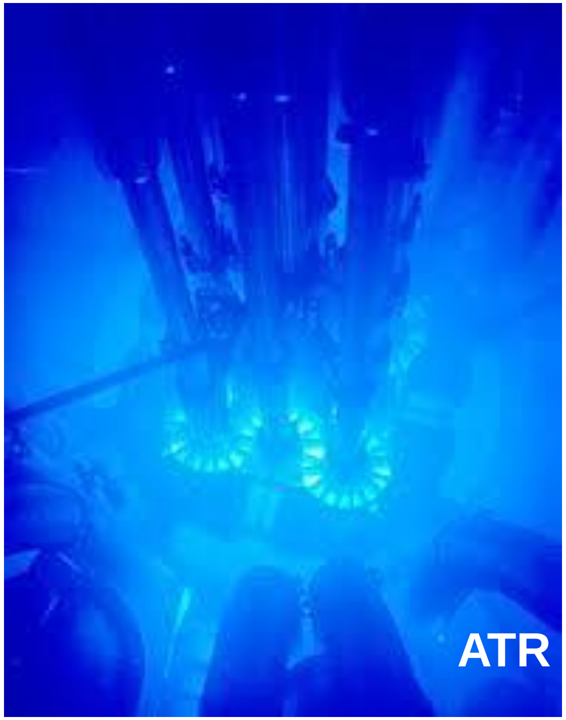
THE NATIONAL ACADEMY OF SCIENCES
IN SERVICE TO THE NATION

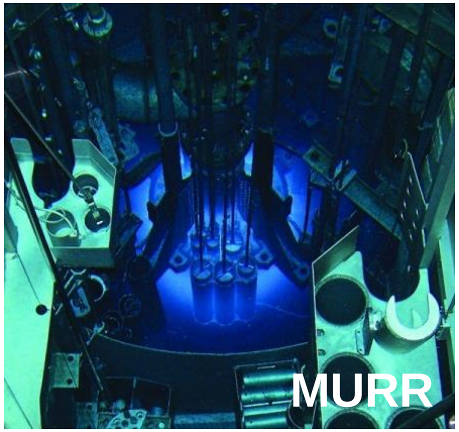
Global Threat Reduction Global Partners

US Dept of Energy CONVERT Program

- **Before the Russians will agree to convert their domestic research reactors, US needs to prove it first.**
  - MIT-R, U. of Missouri (MURR), NIST, ATR (INL), HFIR (ORNL)
- **Convert from highly enriched uranium fuel (vulnerable) to monolithic low enriched U-10Mo fuel plates.**
- **Most of these reactors use dispersion fuels, i.e. bound powder compared to solid plate**







US Dept of Energy CONVERT Program

- **DOE and NNSA established the Office of Material Management and Minimization (M^3) CONVERT Program to support non-proliferation, by replacing vulnerable high enriched nuclear fuels with low enriched, non-weapons-useable, fuels (U-10Mo).**
- **Fabricating and certifying new fuel is team of National Labs and Industry**
- **LANL's primary mission is plasma spray Zr diffusion barrier on U-Mo fuel and Al clad.**
- **LANL also plays a large role in casting the U-Mo alloy**

Idaho National Laboratory

Pacific Northwest NATIONAL LABORATORY

Y12 National Security Complex

BWXT BWX Technologies, Inc.

Los Alamos NATIONAL LABORATORY EST. 1943

Diffusion

- **Metals, in contact, will diffuse.**
- **Rate of diffusion is based on temperature and time.**

$$D = D_0 e^{E_A/kT}$$

$$\frac{\partial c}{\partial t} = D \cdot \nabla^2 c \longrightarrow \frac{\partial c}{\partial t} = D \cdot \frac{\delta^2 c}{\partial z^2}$$

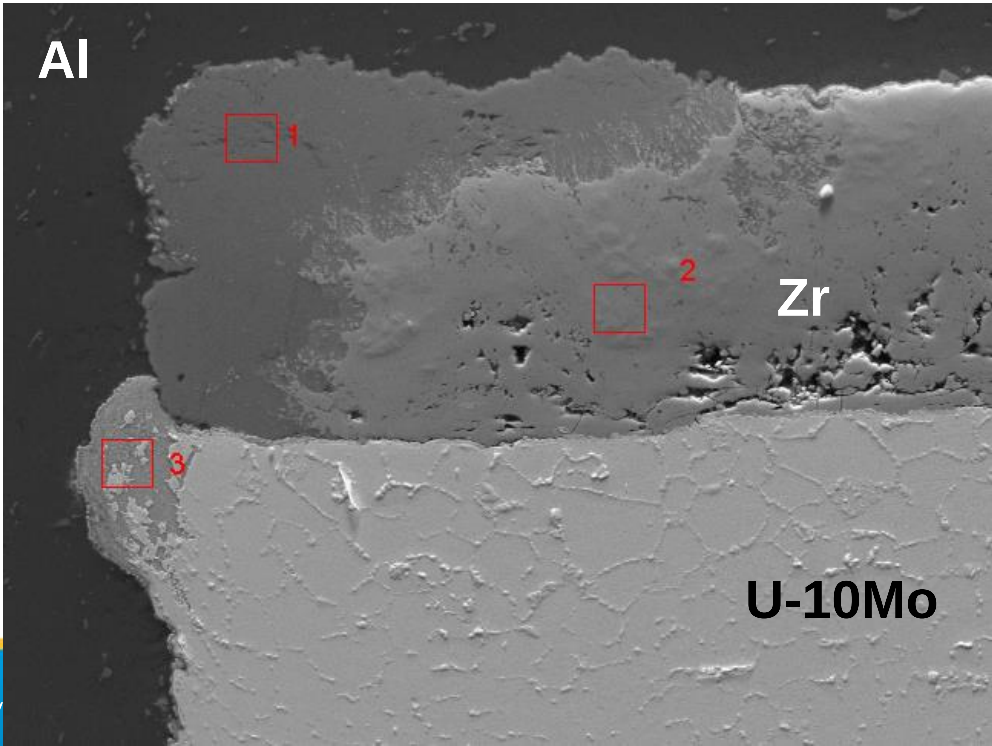
- **In the case of U-10Mo clad in Al, U, Mo and Al all interdiffuse under reactor conditions.**
- **In U-10Mo, uranium diffuses ~10x faster than Mo, which leads to Mo segregation**
- **D_U = 2.60E-15 D_{Mo} = 2.59E-16 @ 650°C (m^2s^{-1})**

Huang, et al. 2013

Zr Diffusion Barrier

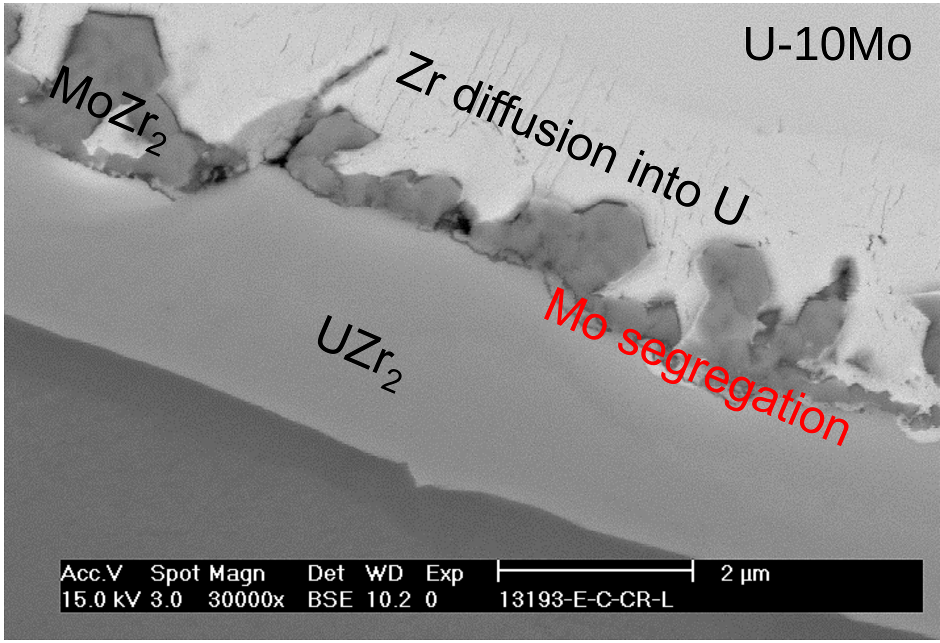
- **Uranium forms a low melting point eutectic with aluminum. Reduced strength, possible contamination**
- **A diffusion barrier should prevent Al-U interactions .**
- **Zr has a high melting point,conductivity, mechanical strength, low neutron absorption.**

	at%		
	Spot 1	Spot 2	Spot 3
Al	72.67	0.43	67.03
Mg	1.95	0.08	0.00
Si	0.00	0.00	4.47
Zr	25.38	99.49	0.13
Mo	0.00	0.00	6.05
U	0.00	0.00	22.32

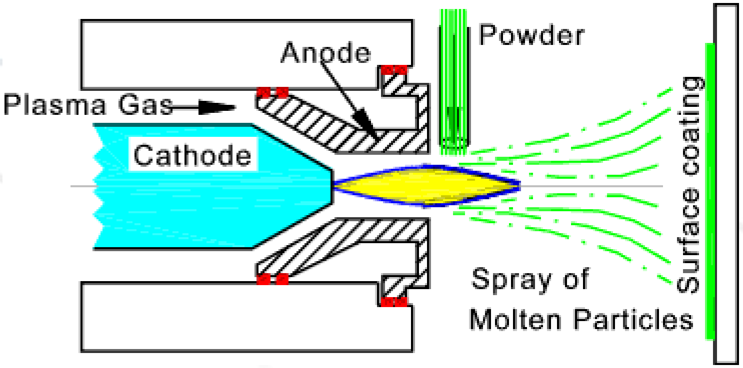


Conventional Hot Roll Bonding

- **Conventional industry uses hot roll bonding to apply thin Zr layers to a nuclear foil.**
- **Held at ~500 to 600°C for long periods and rolled to bond layers.**
- **High temperature and pressure from rolling leads to phase segregation, diffusion, strain, eutectics, etc.**

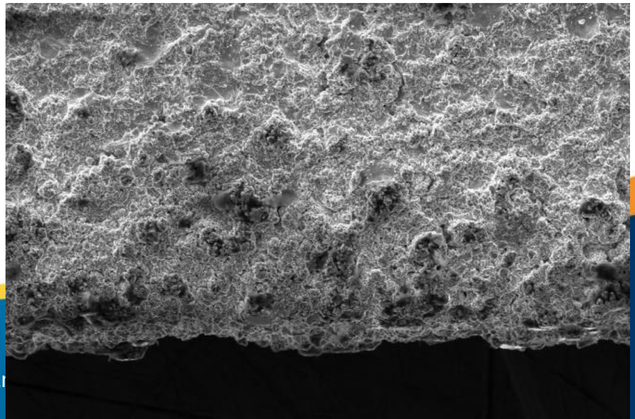


Plasma Spray Process



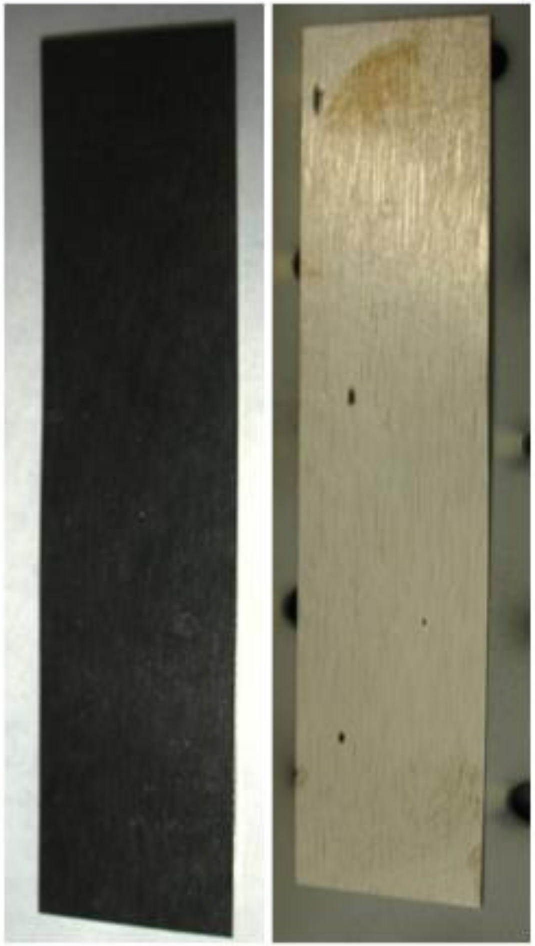
Beardmore, R.; www.roymech.co.uk; 2013

- **Thermal Spray utilizes a "gun" to heat a powdered material (metals or ceramics) and accelerate those molten particles toward a substrate, where the particle deforms to create a layered coating.**
  - Plasma spray utilizes a DC plasma torch as the heat source. Plasma temperatures reach ~15,000°C
- **Multiple passes of the torch deposit one layer at a time, building up the thickness of the final coating.**
- **Efficient method commonly used in industry for coatings.**

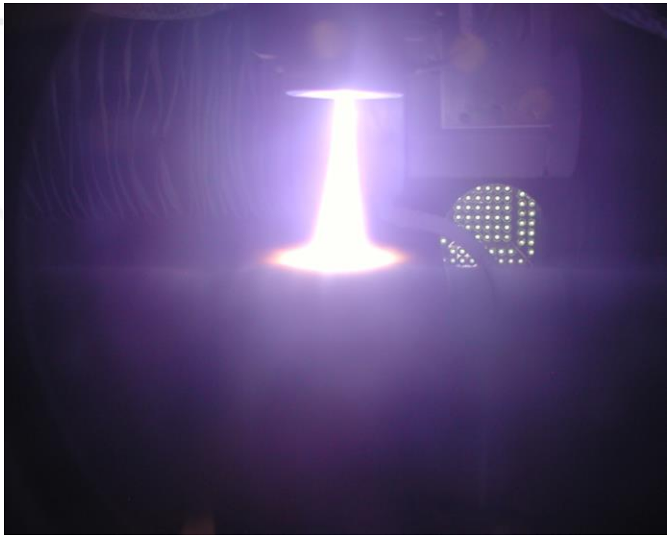


Processing Steps for Plasma Sprayed Zr

- **First, the U-10Mo is cleaned by a strong basic solution, rinsed, then placed in strong acid**
  - Removes black oxide layer and cleans surface.
- **These cleaned foils are loaded onto a 4-sided fixture, held by adjustable screws.**



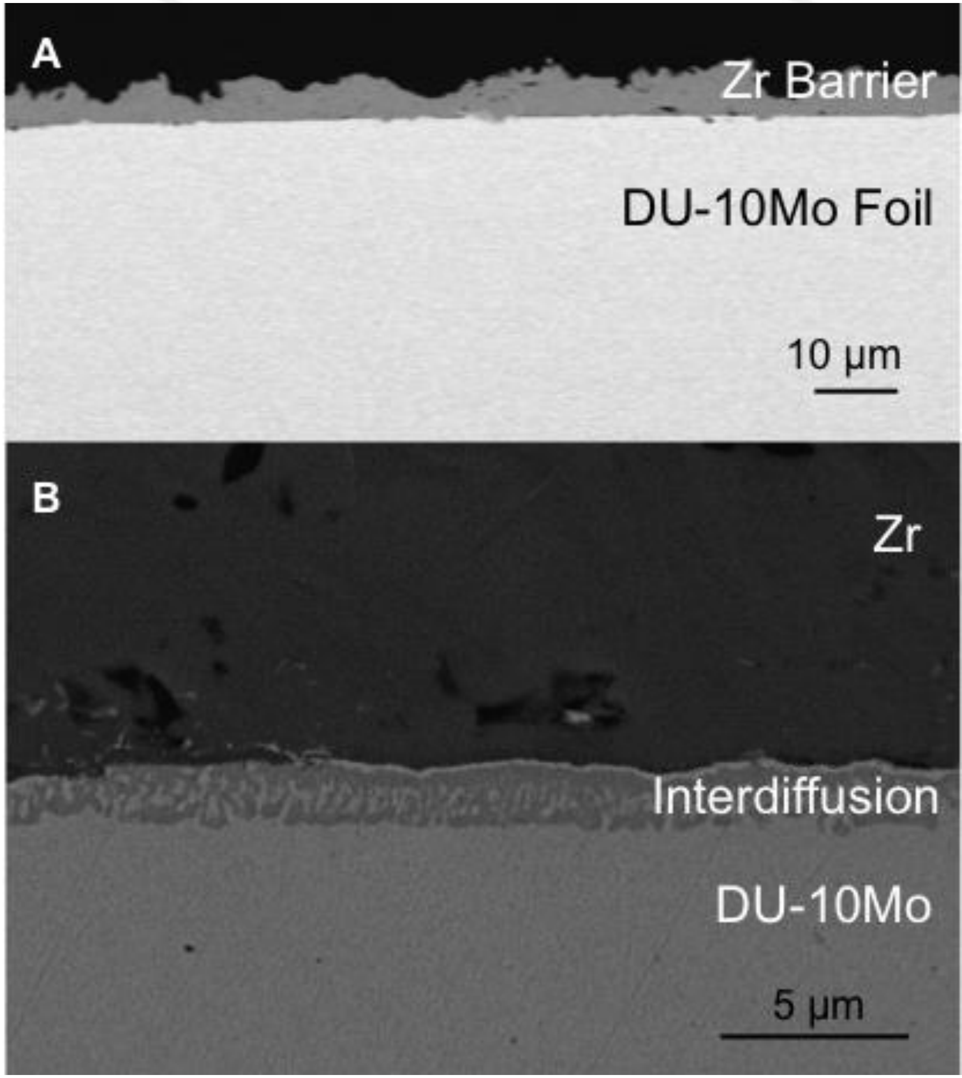
Plasma Spray Process



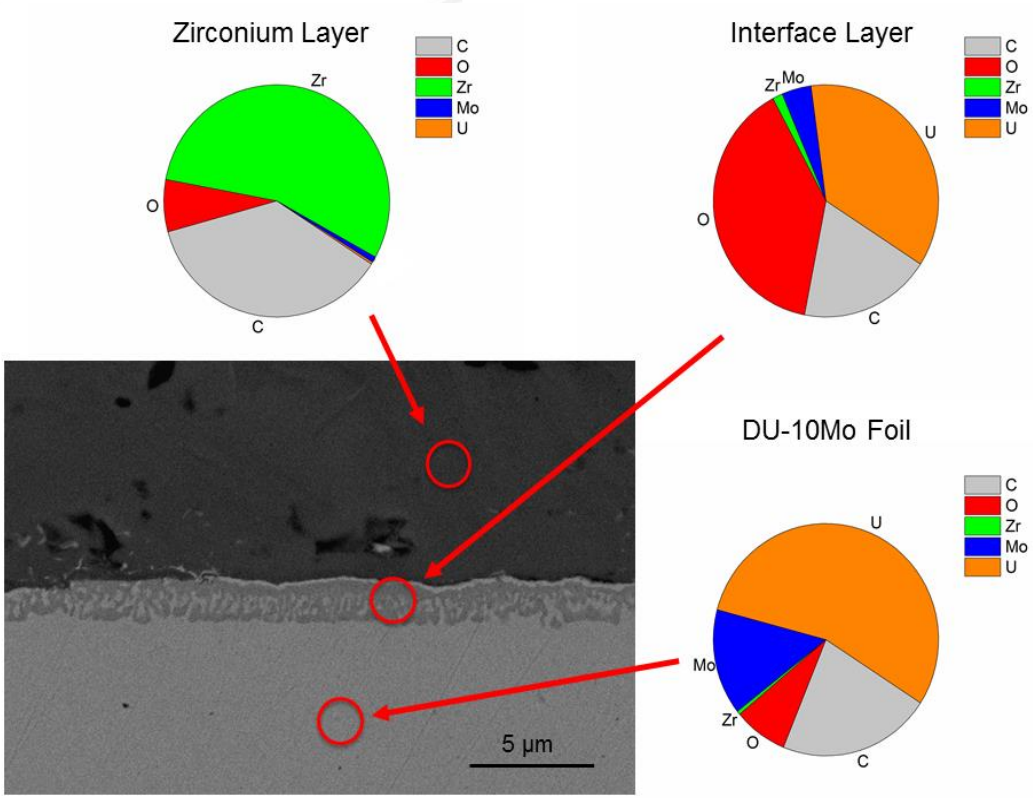
- **DU-10Mo foils are mounted on each side of a square, rotating fixture, which allows for processing 4 foils at once.**
- **System is evacuated, then backfilled with ~70 Torr Ar, to reduce oxidation during spraying.**
- **DU-10Mo foils are sprayed with Zr powder (5 – 50 μm) injected into Ar-He plasma, with plasma power of ~25 - 30kW. Substrate reaches 500 to 800°C quickly.**

Zr – DU Interface Layer

- **Clearly defined interface layer between Zr coating and DU-10Mo foil.**
- **Layer thickness is relatively uniform across width of the foil.**
- **SEM/EDS Elemental Analysis and WDS Microprobe (more sensitive) show oxygen rich layer at surface**



Interfacial Layer Elemental Analysis

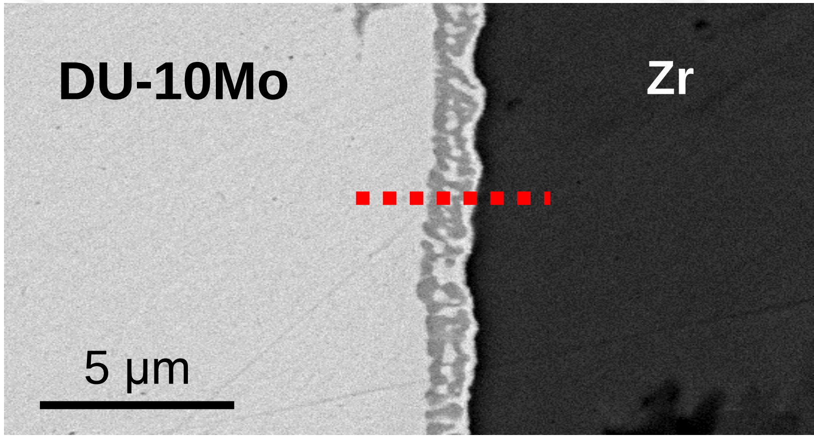


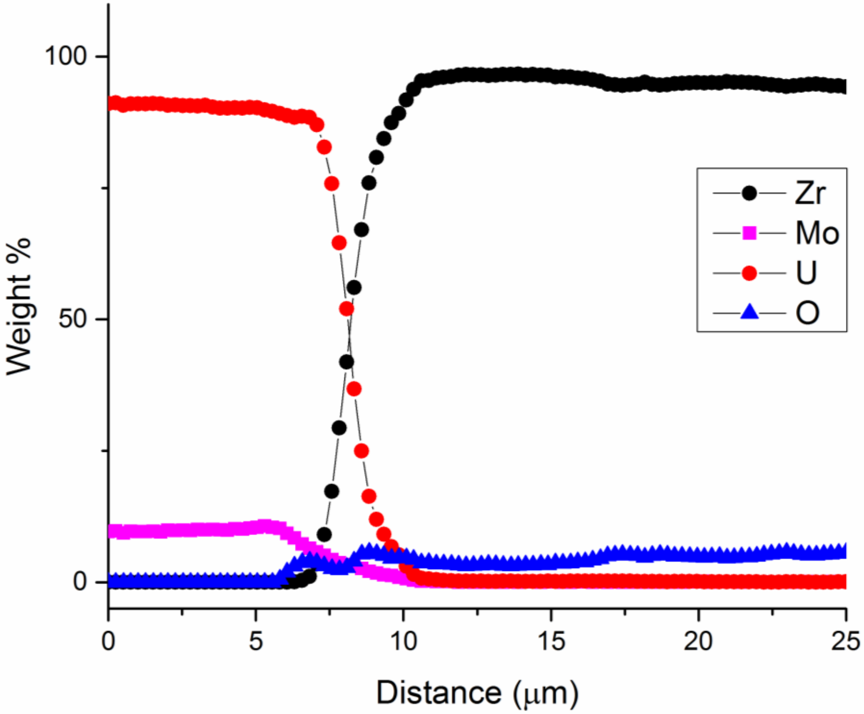
EDS Element	Zr Barrier	DU-10Mo	Interface
C K	36.52%	21.99%	0.19%
O K	7.29%	7.75%	39.15%
Zr L	55.06%	0.50%	1.44%
Mo L	0.81%	14.76%	4.21%
U M	0.32%	55.00%	36.31%

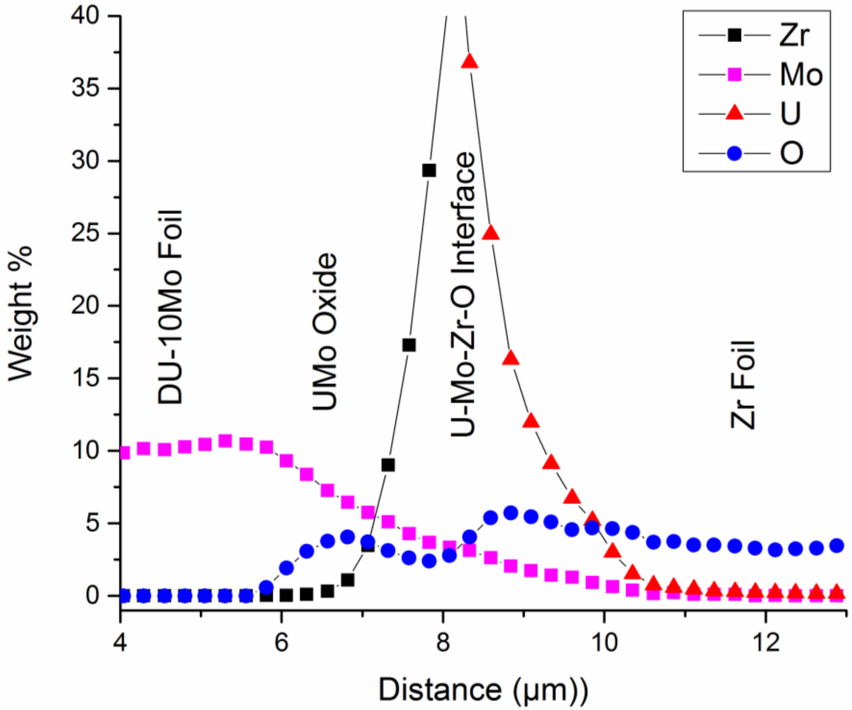
- EDS Elemental analysis shows Zr layer and DU-10Mo foil are mostly pure with minimal oxidation, which is expected.
- Analysis of interface shows U-Mo with Zr, but significant oxygen.
- Sample coated in Carbon.

WDS Microprobe Analysis of Interface

- **WDS provide quantitatively elemental analysis**
- **Oxygen calculated by difference.**
- **Seems to suggest interface layer and U surface oxide.**



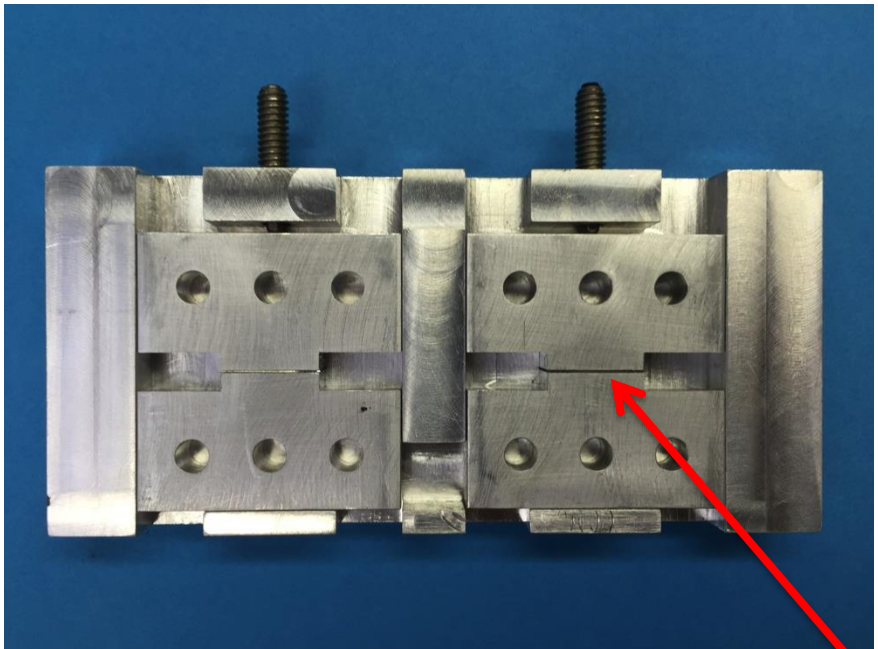




Tensile Test for Bond Strength Evaluation

MST-8: C. Liu, M. Lovato, J. Valdez

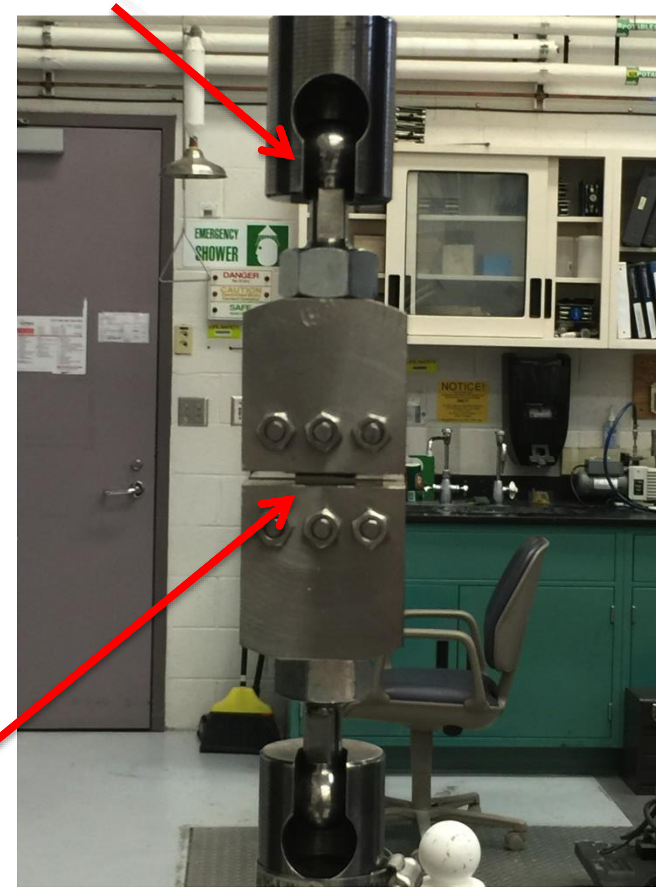
Tensile test samples are 9.5 mm x 19 mm



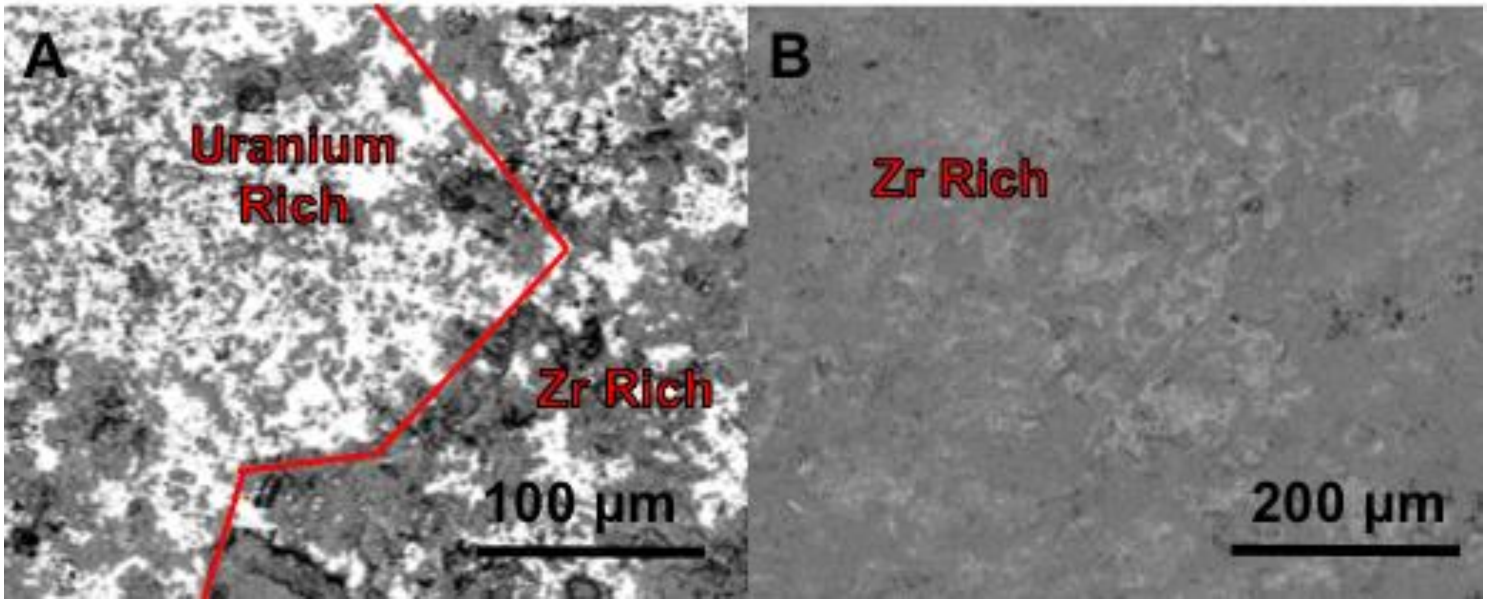
Fixture for epoxy curing
to mount foil for testing

Mounted Foil

Ball joints eliminate any bending and twisting.



Bond Strength

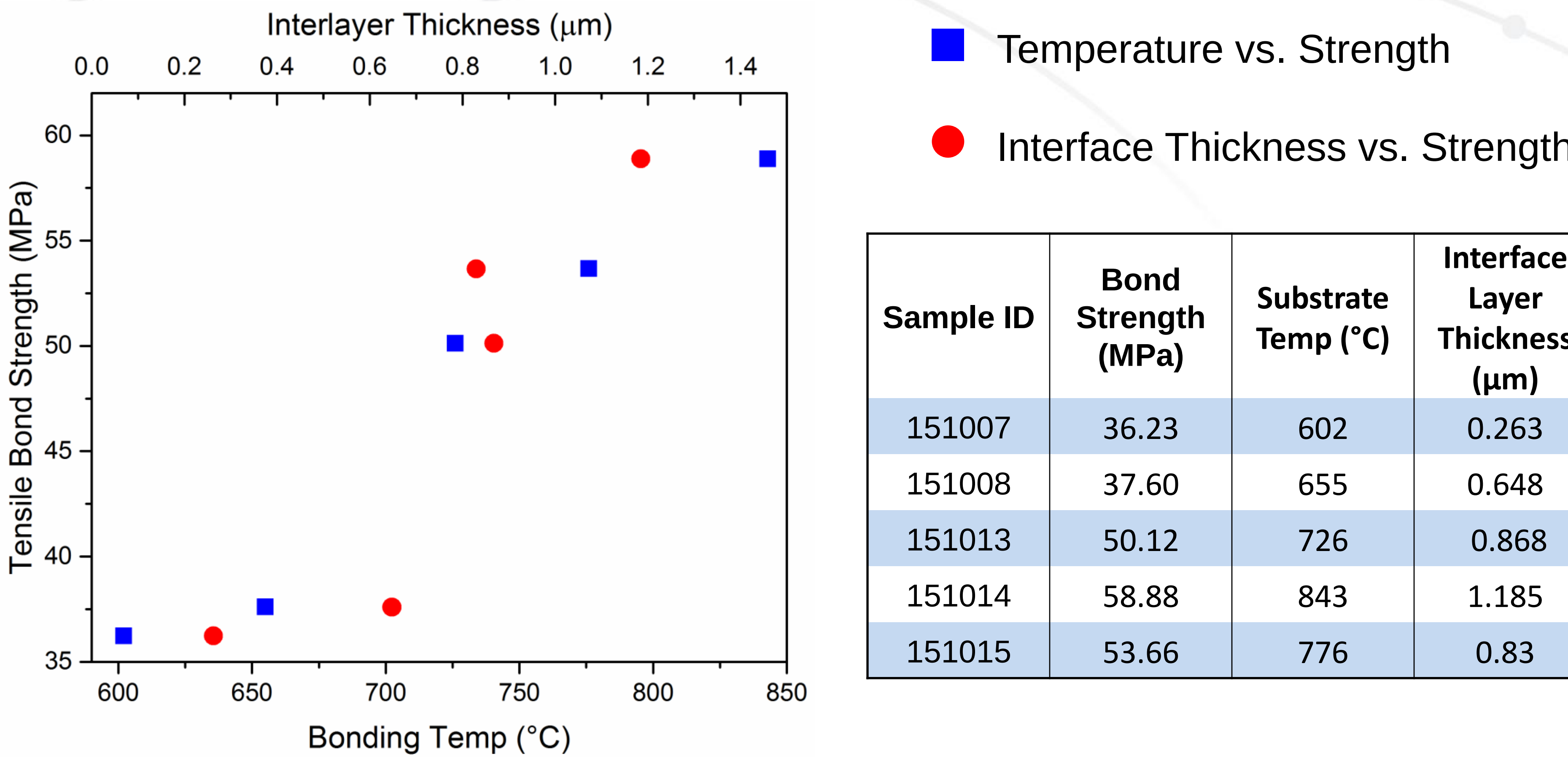


151007-1 "Weakest" Sample

151014-1 "Strongest" Sample

- **"Strong" bond strength shows fracture between adhesive and Zr coating**
- **"Weak" bond shows fracture between Zr and U**

Temperature/Bond Strength Relation

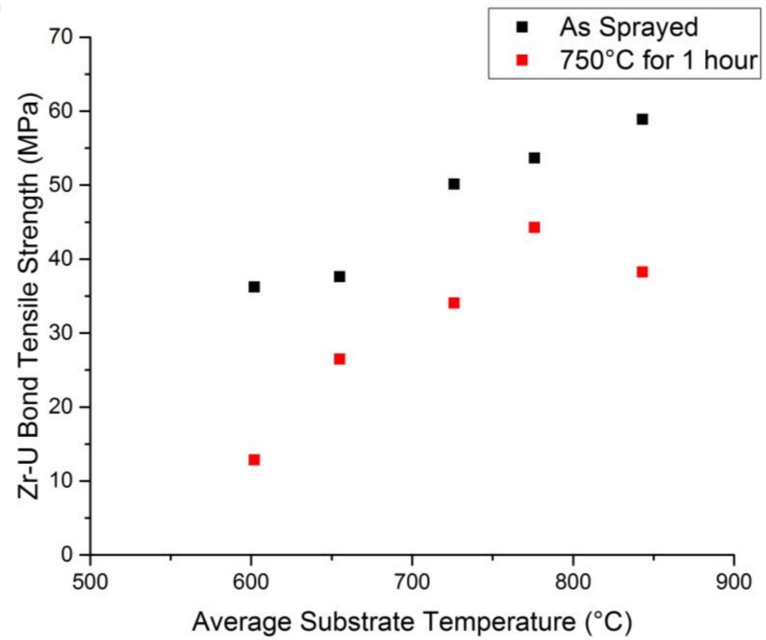


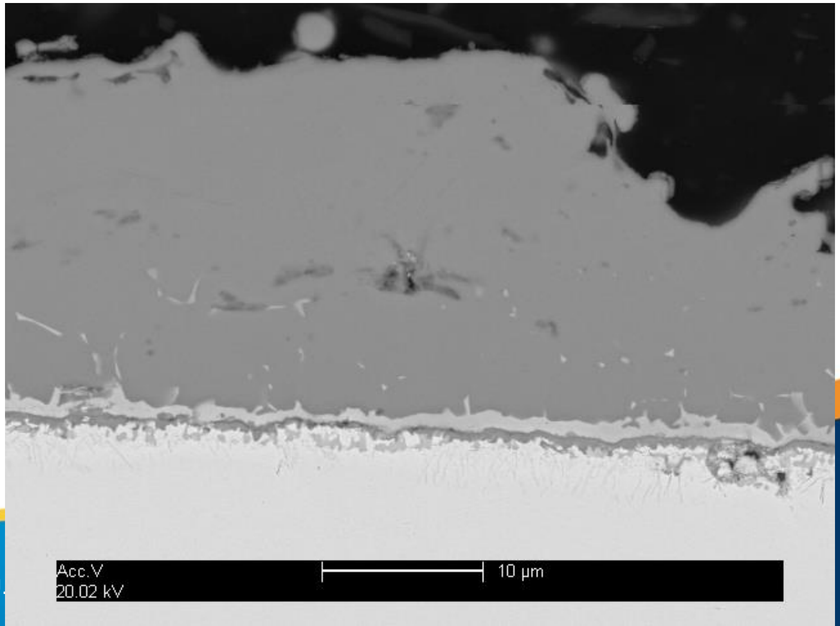
Sample ID	Bond Strength (MPa)	Substrate Temp (°C)	Interface Layer Thickness (μm)
151007	36.23	602	0.263
151008	37.60	655	0.648
151013	50.12	726	0.868
151014	58.88	843	1.185
151015	53.66	776	0.83

- **Clear correlation between bonding temperature, interface thickness, and bonding strength.**
- **Average substrate temperature determined by IR camera during spraying**

Plasma Spray Zr Adhesion – Heat Treatment

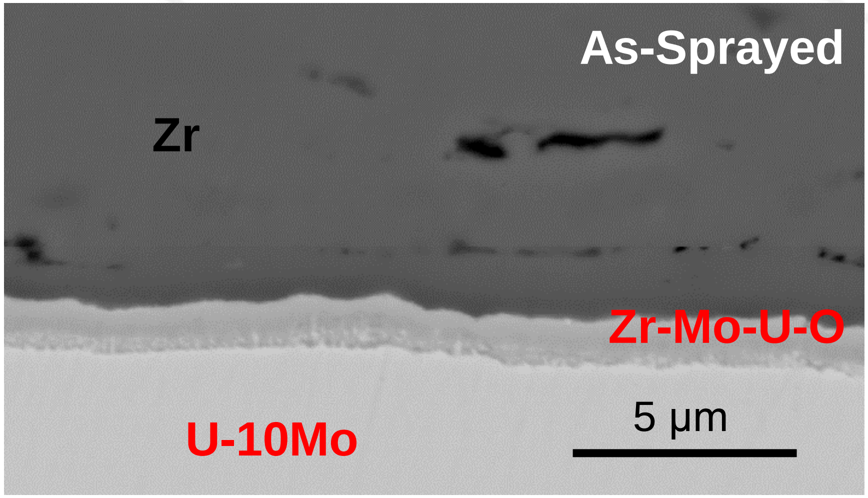
- **The same plasma sprayed foils were placed in an Ar atmosphere and heat treated at 750°C for 1 hour.**
- **Following heat treatment, all plasma sprayed samples showed lower adhesion (Red Squares).**

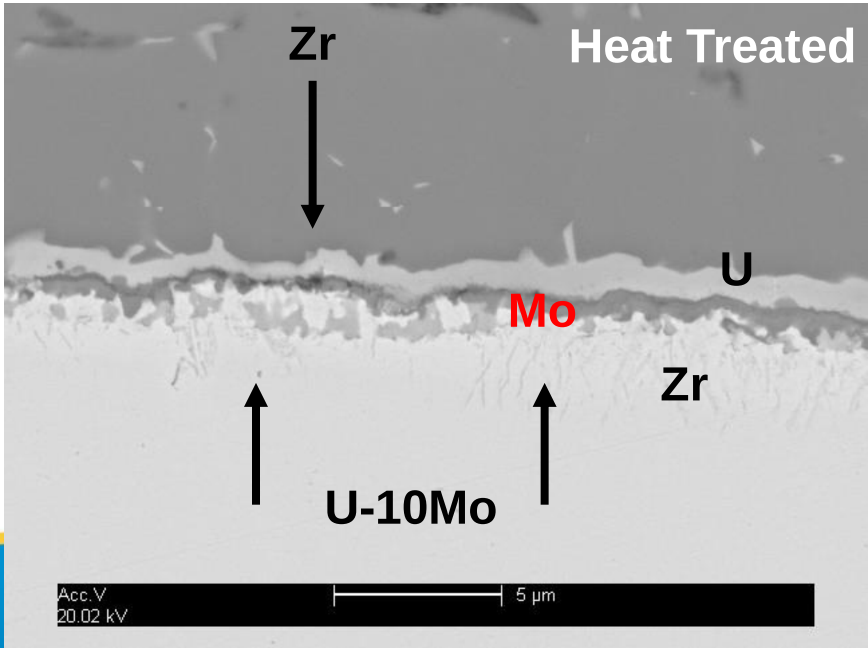




Plasma Spray Zr Adhesion – Heat Treatment

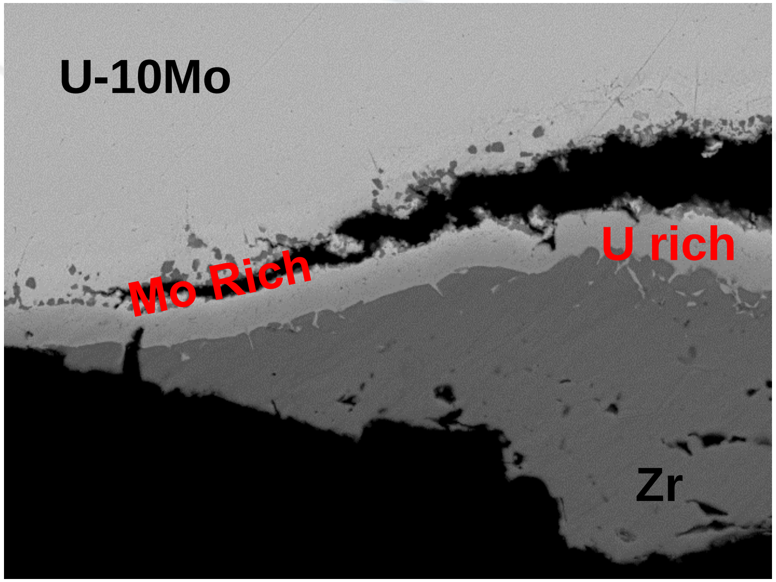
- After heat treatment, Zr continues to diffuse into bulk of U foil, and U diffusing into the Zr coating.
- Molybdenum segregates at the interface.
- Interface and Segregation looks similar to hot-roll bonded materials.

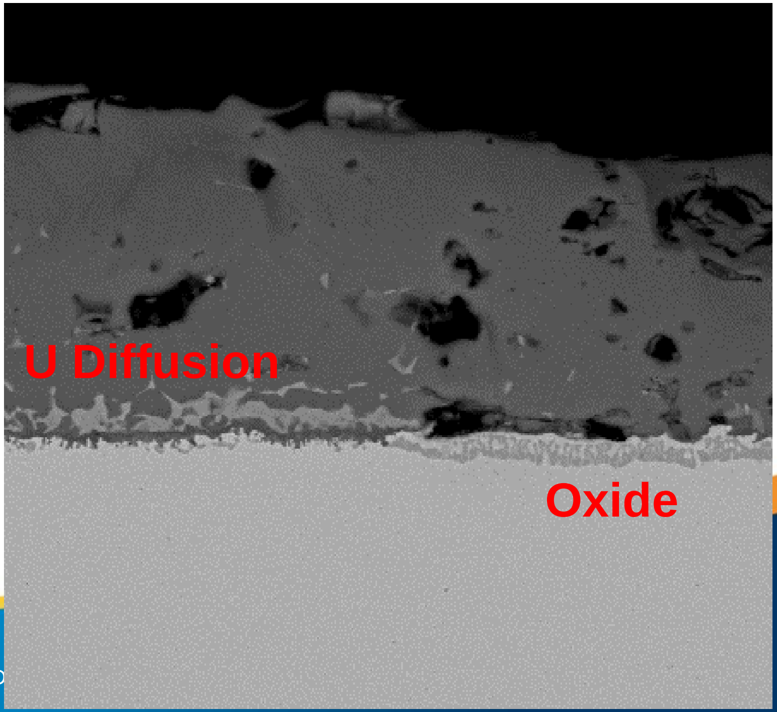




Plasma Spray Zr Adhesion – Heat Treatment

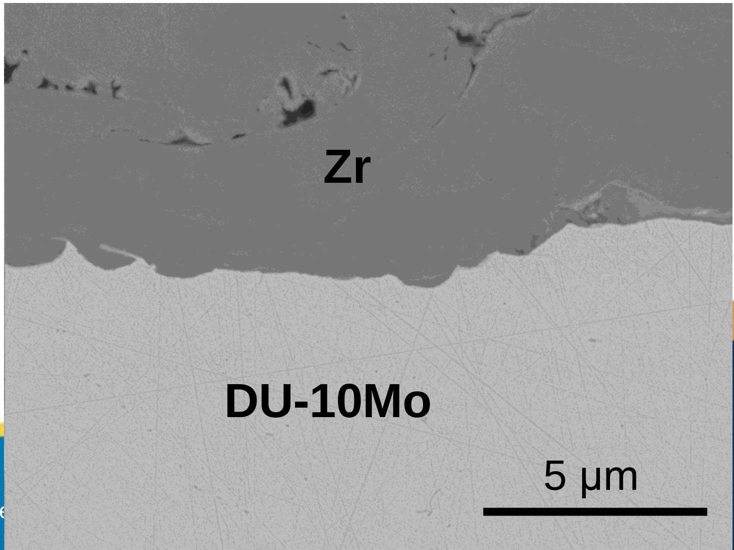
- **Metallographic analysis shows accumulation of Mo and U diffusion into Zr following heat treatment.**
- **Fracture tends to occur at Mo rich interface. Similar interface to roll bonding**
- **Seems that oxygen rich layer limits Mo and U diffusion during heat treatment.**



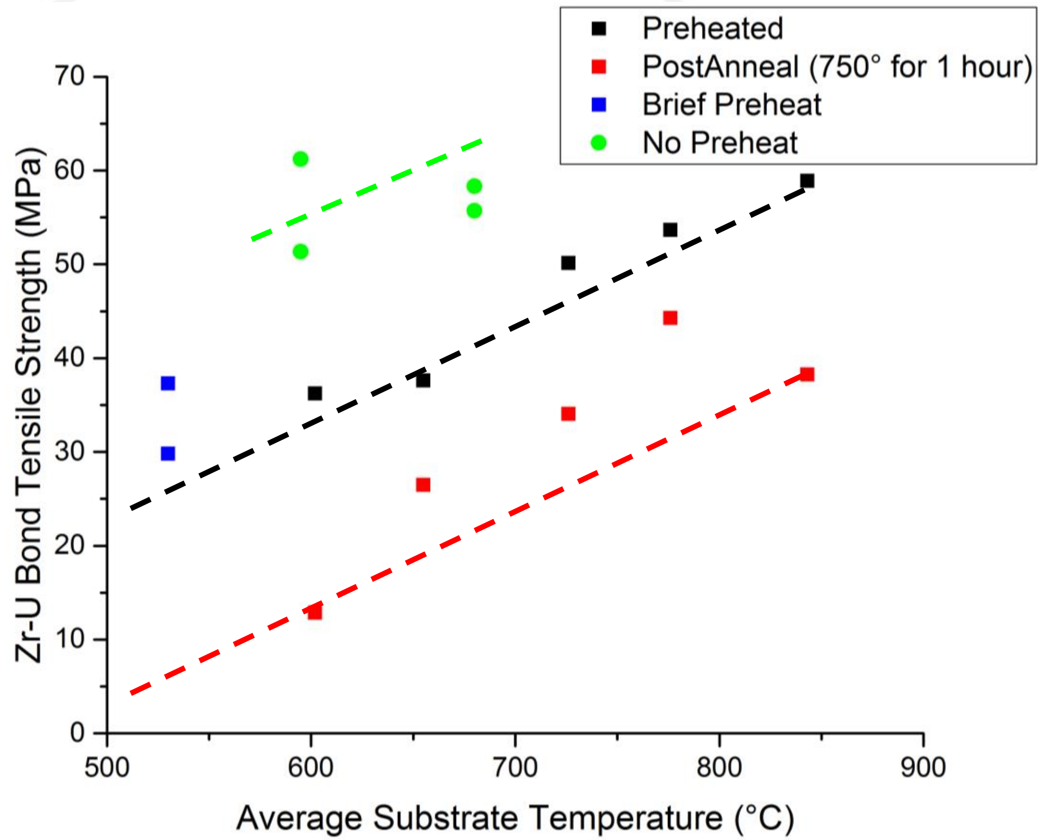


Reducing Oxidation

- Since the weakest point seems to be at the U-oxide – Zr interface, eliminating oxidation will improve integrity.
- Reduce “pre-heating” and start depositing Zr immediately and heating afterward.
- Appears to be no oxide layer and minimal U diffusion into the Zr.
  - U surface roughness is present after cleaning process prior to spraying



Bond Strength



- **Reduction of oxidation at the Zr-U interface seems to improve bond strength**

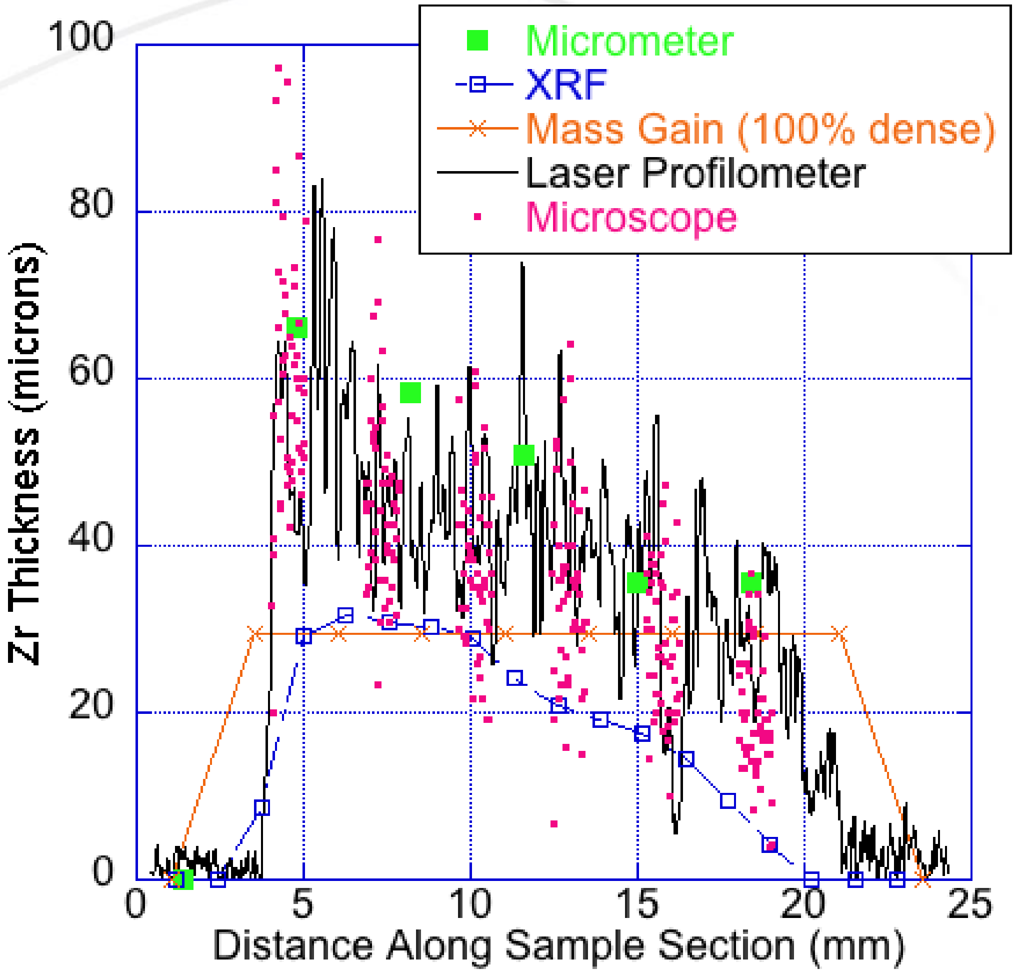
Quality Assurance

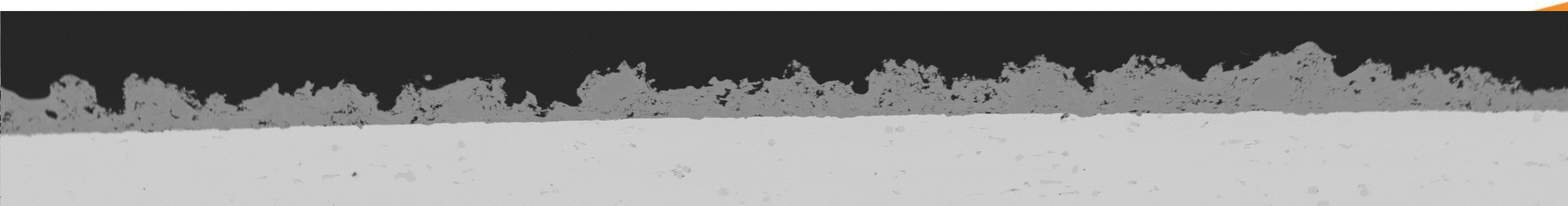
- This will be one of the first new fuels qualified by the NRC in over 30 years.
- Requires stringent quality assurance practices and documentation (NQA-1)
- Not trivial to transfer basic scientific, R&D, and experimental practices to the same quality control as commercial nuclear reactors.
- Even measuring the coating thickness is much harder than it sounds…

Thickness measurements

- **The customer's final specifications focus on the final Zr thickness.**
- **How do you accurately, reliably, and repeatably measure a ~30 micron metal coating on a radioactive foil?**
- **What other factors are important?**
- **Multiple techniques:**
  - Mass gain
  - Micrometer
  - Metallography/Microscopy
  - XRF
  - Laser Profilometry
  - Spectroscopy

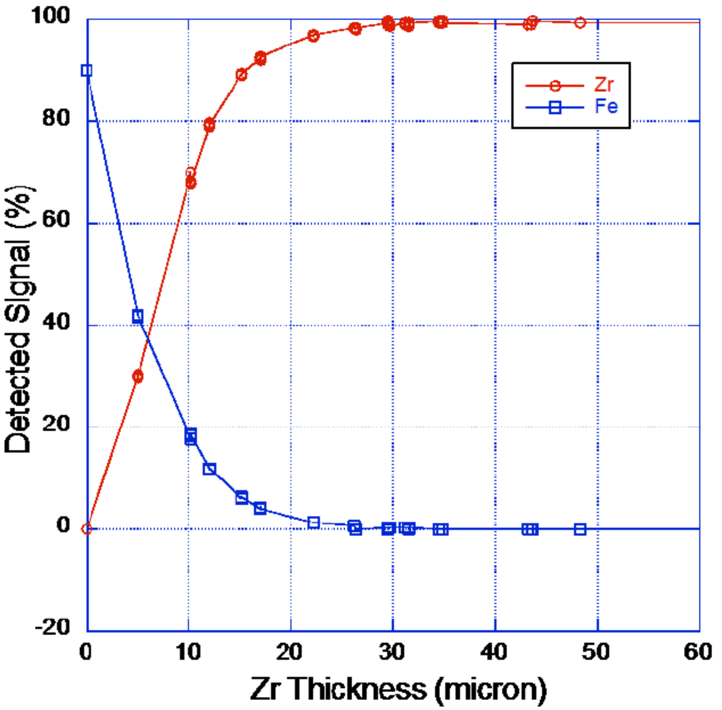
Technique Comparison Zr on SS



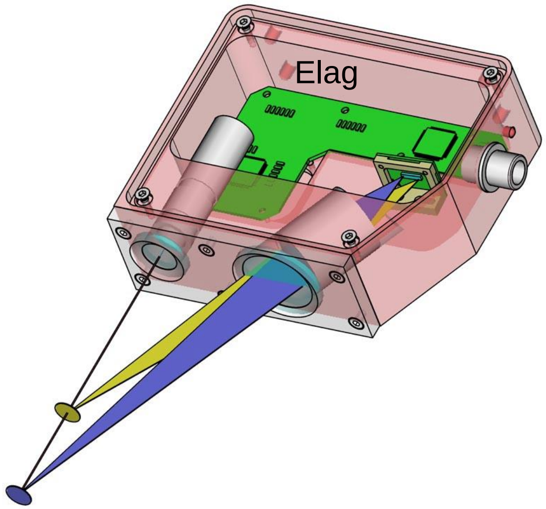


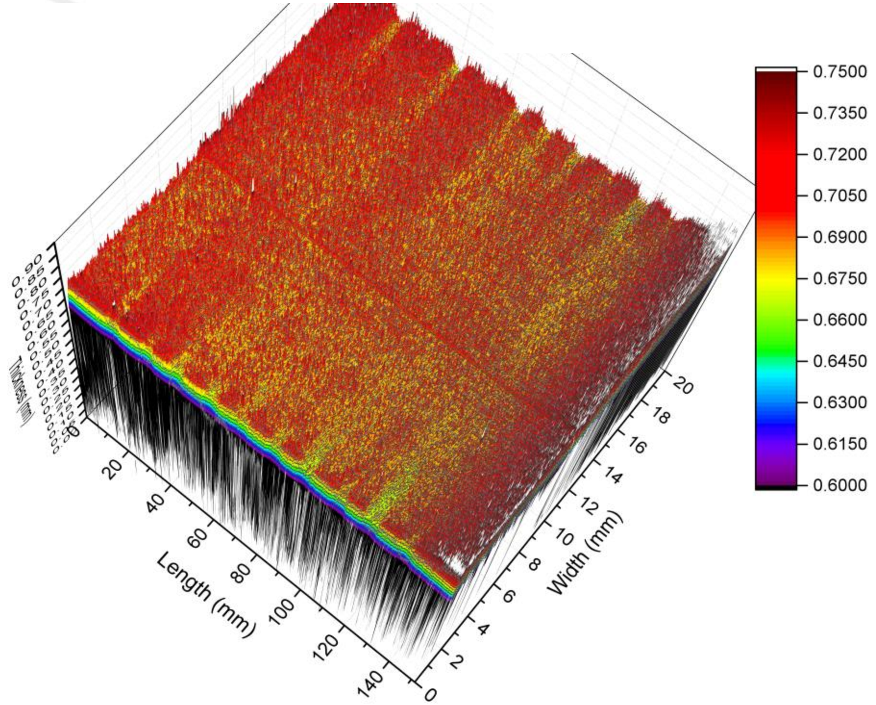
XRF

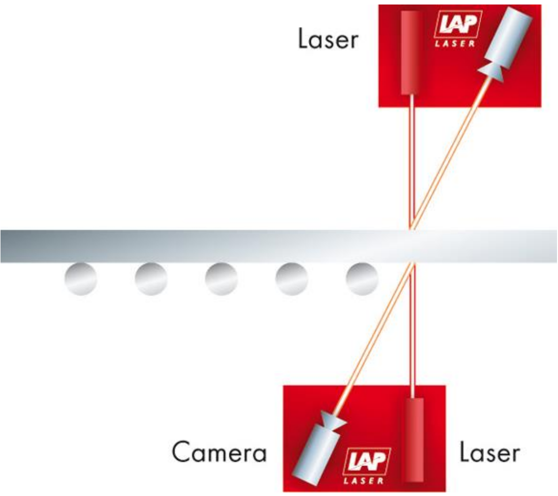
- X ray Fluorescence operates by bombarding a sample with high energy x rays, then measureing the emitted secondary x-rays.
- For thickness, measurements are skewed toward thicker portions and require calibration curves.
- X-rays can only penetrate thinner coatings, so technique is quickly saturated.



Laser Triangulation Thickness Measurements







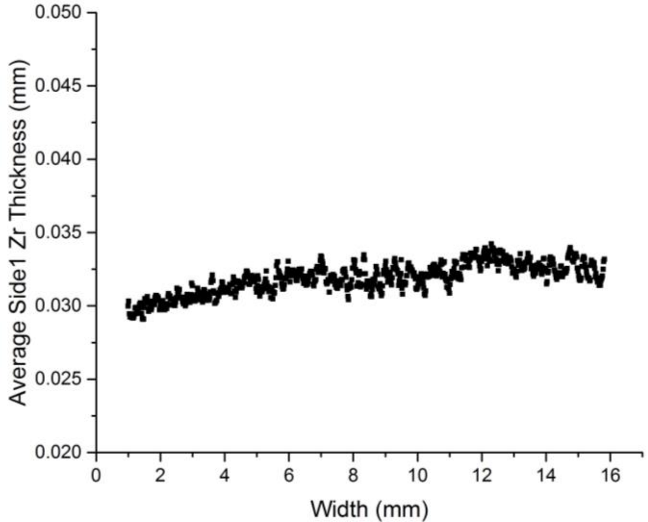
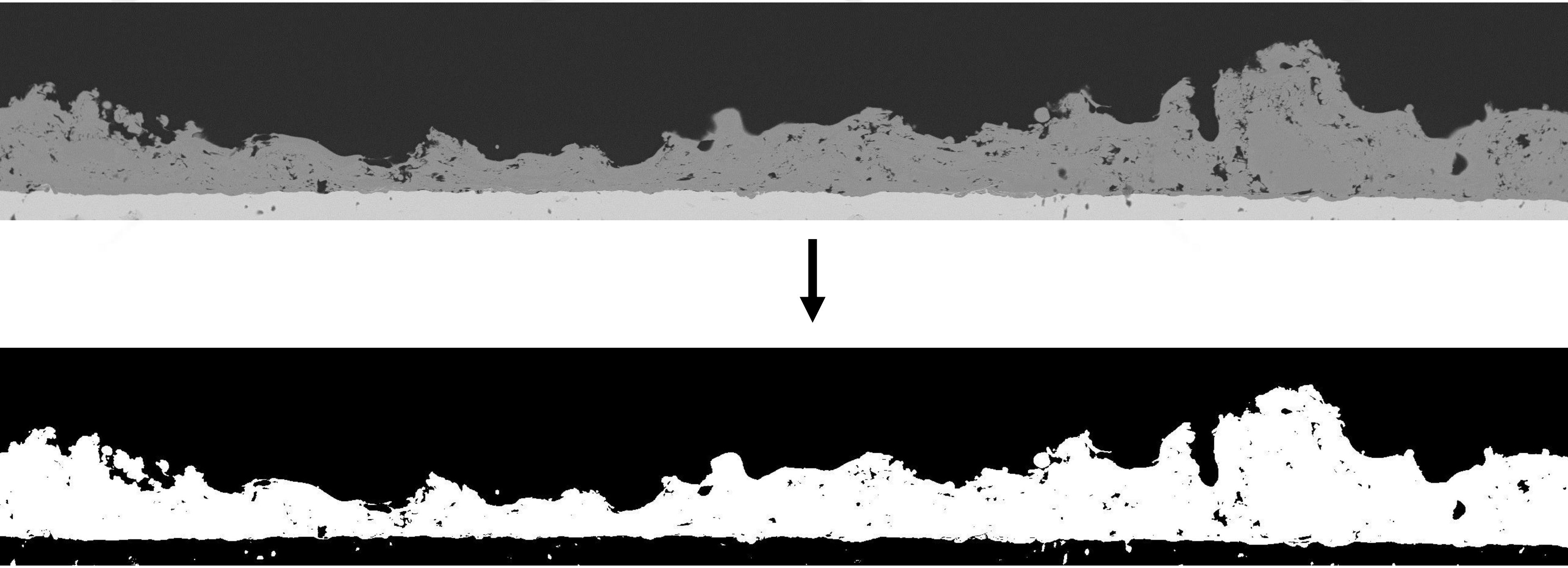


Image Analysis



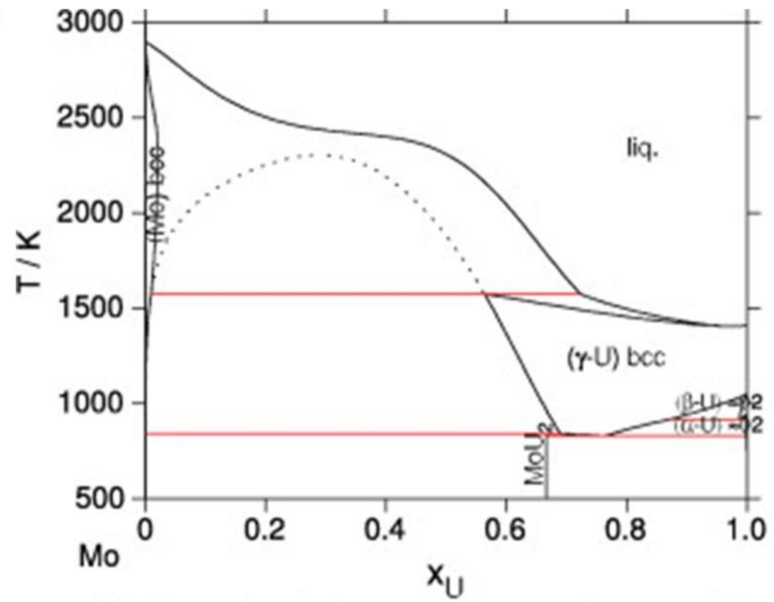
- Backscattered SEM image of metallographic cross section
- Convert image to binary, then average thickness over set interval.

Neutron Diffraction for α/γ Phase Fractions

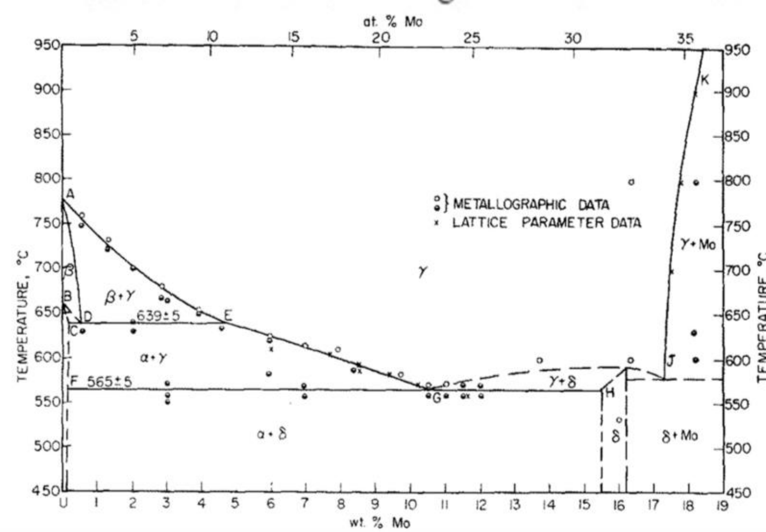
Sven Vogel, Don Brown – MST-8

- **More conventional XRD cannot penetrate the uranium fuel, especially with eventual cladding. Destructive metallography is time consuming and can be technician dependent.**
- **The gamma to alpha transition (BCC to orthorhombic) occurs at ~565°C**
- **γ-U swells isotropically under irradtion and has stronger mechanical properties**
  - α-U swells anisotropically, so unpredictable expansion, stresses, etc.

A)



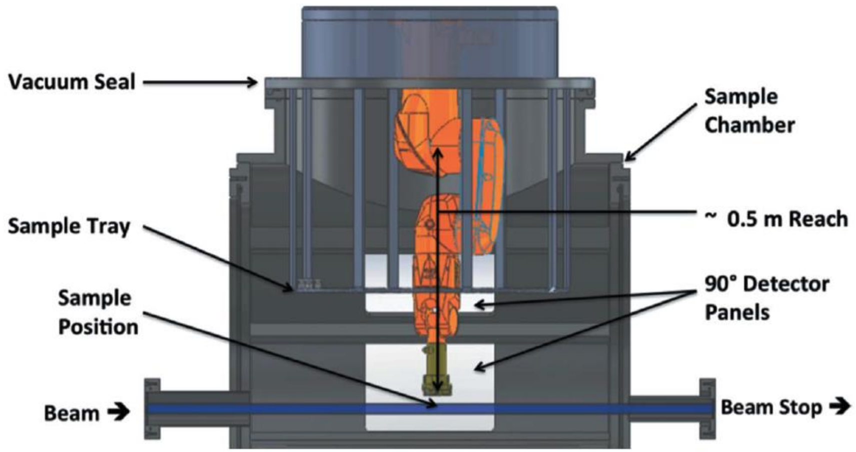
B)



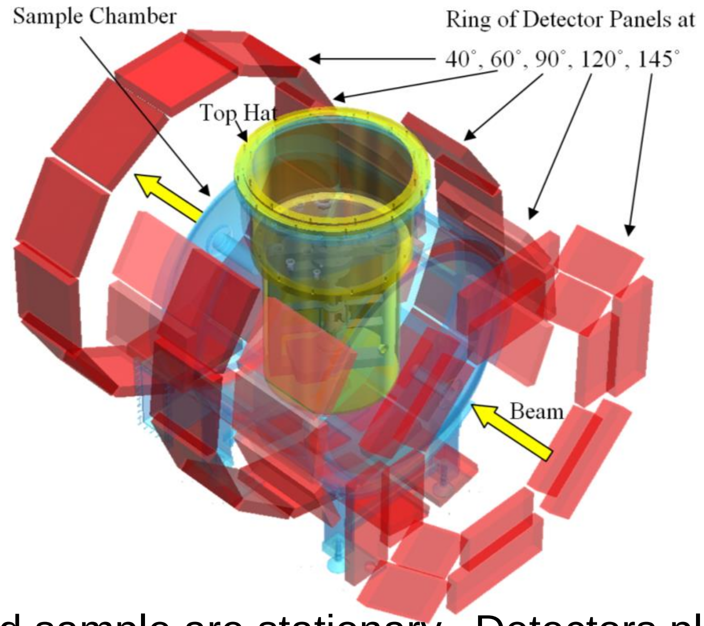
Neutron Diffraction for α/γ Phase Fractions

Sven Vogel, Don Brown – MST-8

- **To determine effects of plasma spray on phase composition of U foil, Neutron Powder Diffraction was performed on 1 bare DU-10Mo foil and 5 Zr plasma spray coated samples in HIPPO.**



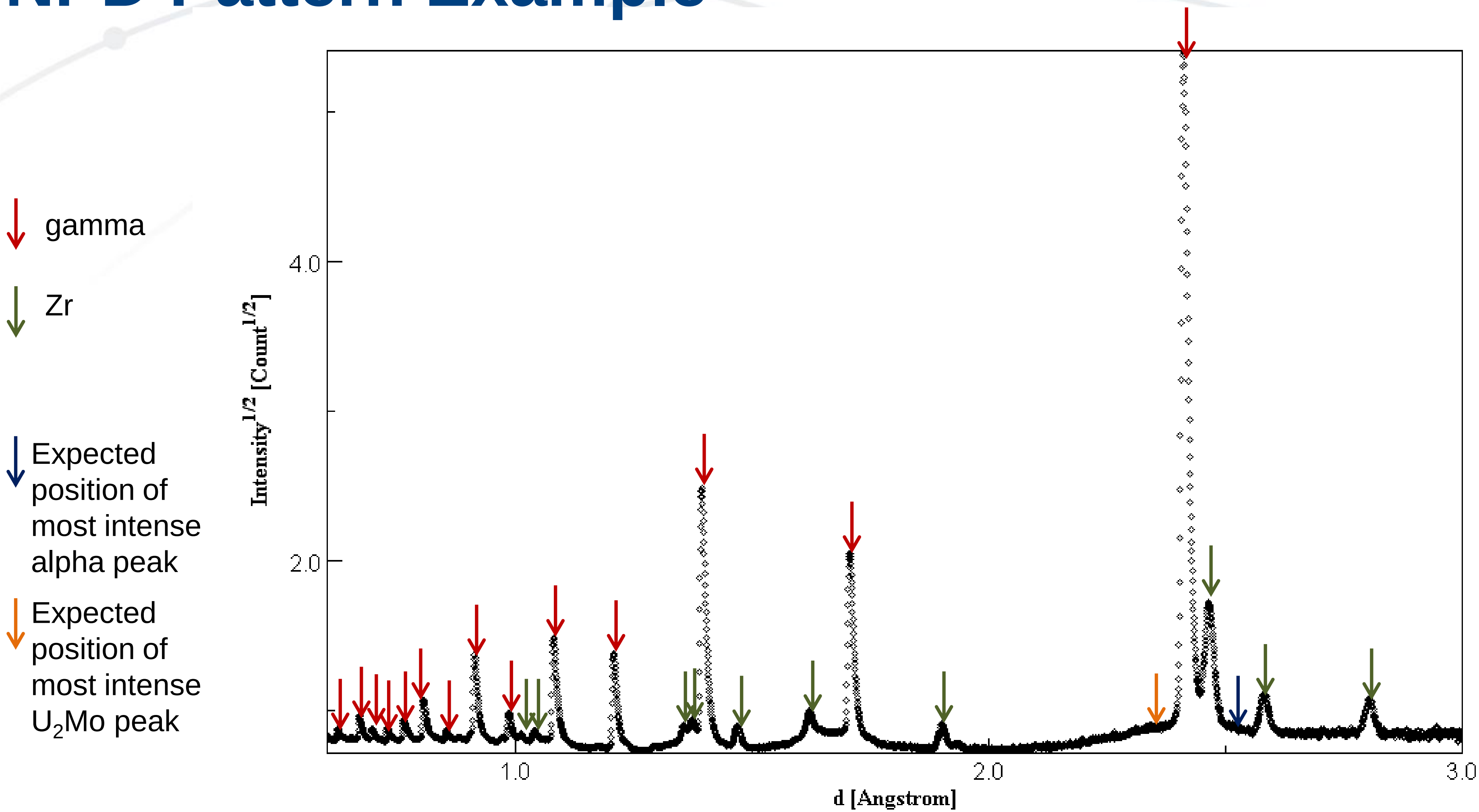
Wenk et al., Nucl. Instr. Meth. A, 515 (2003) 575-588 Losko et al. J. Appl. Cryst. (2014). 47, 2109–2112



Beam and sample are stationary. Detectors placed at various angles determine diffraction behavior.

The sample tray can hold ~100 samples which are loaded into the beam automatically 24/7. Each sample requires 1-2 hours for a good spectrum.

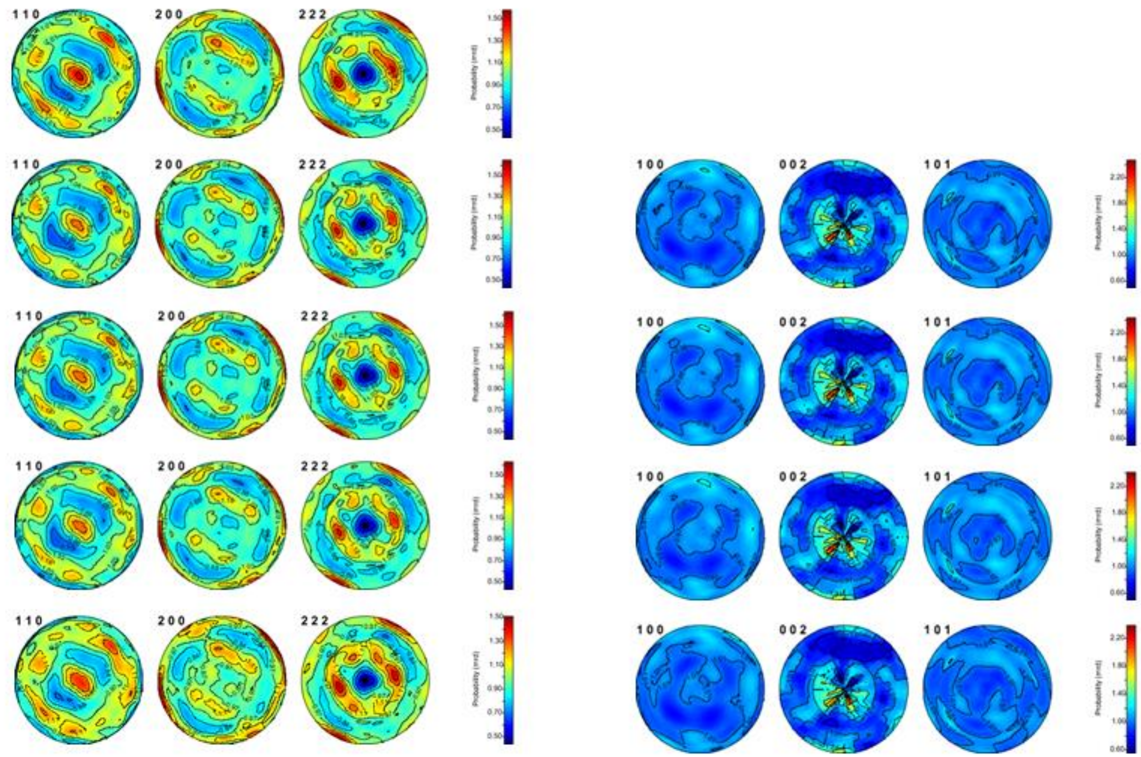
NPD Pattern Example



NPD shows that bare DU-10Mo is ~100% γ-phase U and no observed phase transition during plasma spraying.

Gamma-U Phase Fraction

- Measurements sensitive to ~0.5 wt% phase composition, with error in the same magnitude.
- Starting DU-10Mo ~1 wt% alpha phase.



- No significant change in plasma spray; slight increase in roll bonding.
- Texture analysis shows no real change in crystalogrpahy following plasam spray

Conclusions

- The conversion of highly enriched uranium fuels in research reactors, is critical to nuclear security and non-proliferation.
- LANL's primary mission for the CONVERT program is the deposition via plasma spray of a Zr metal diffusion barrier between the U-10Mo fuel plate and eventual Al cladding
- Results show plasma spray is an efficient and reliable method as a part of nuclear fuel plate production.

Acknowledgement

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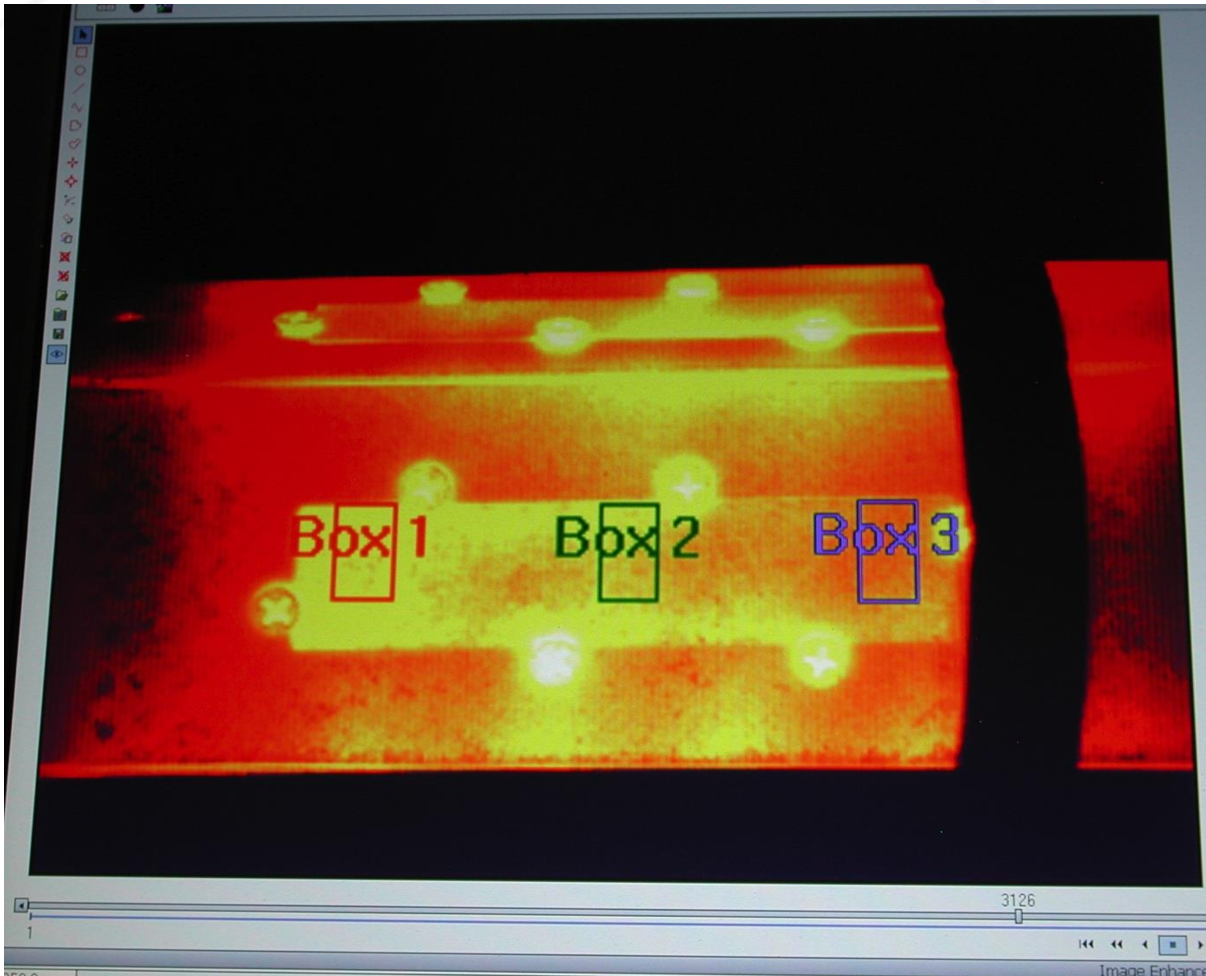
Back Up Slides

IR Surface Temperature Measurement

Average temperature calculated at ends and center of sample



Temperature Data and Peak Cycle Averaging

Average of peak cycle = 843C